

COMPLEXES OF ACID AMIDES WITH POLAR APROTIC SOLVENTS. I.

COMPLEXES OF BIS(N-PHENYL)-PYROMELLITIC ACID DIAMIDE WITH DIMETHYLFORMAMIDE

YU. N. SAZANOV, L. A. SHIBAEV, S. A. DAUENGAUER, A. N. KRASOVSKY and
K. K. KALNINSH

*Institute of Macromolecular Compound of the Academy of Science of the U.S.S.R.,
Leningrad, U.S.S.R.*

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Complexes of bis(N-phenyl)-pyromellitic acid diamide with dimethylformamide were synthesized and studied by thermal mass-spectrometry. It was found that, depending on the precipitating agent applied, the composition of the complexes corresponded to 1 acid amide: 2 dimethylformamide or to 1 acid amide: 1 dimethylformamide. The effects of complex formation on the thermal cyclodehydration of bis(N-phenyl)-pyromellitic acid diamide and on the accompanying degradation processes are discussed.

Complex formation with the participation of polar aprotic solvents plays an important part in all stages of aromatic polyimide syntheses. The starting monomers, in particular dianhydrides, form fairly stable complexes with dimethylformamide and other amide solvents [1, 2]. It was found that the reactivity of these complexes in the acylation of aromatic amines is lower than that of the initial dianhydride [3]. The complexes of the solvents with the poly(acid amide) formed in the first stage of the synthesis have been studied to a lesser degree, although significant effects of the complex formation on the kinetics of polycondensation [4] and also on the subsequent cyclodehydration of the poly(acid amide) are observable [5].

In the present paper, results of the separation of stable, solid complexes of dimethylformamide (DMF) with bis(N-phenyl)-pyromellitic acid diamide (PMA) and of the determination of their stoichiometric compositions are reported for the first time. PMA may be considered as a model of the basic unit of poly(acid amides). In this paper we also discuss the aspects of decomposition of these complexes and the cyclodehydration process of PMA, using the results of mass-spectrometric thermal analysis.

Experimental

Preparation of PMA–DMF complexes

The PMA–DMF complexes were prepared by the reaction of pyromellitic dianhydride with aniline in DMF under dry argon for 1 hour. The solution of the acid amide formed in the reaction was poured into the precipitating agent,

applied in an excess of 20 : 1. The precipitating agents used were benzene, acetone and water, and the corresponding products were termed complex I, II and III, respectively. Depending on the nature of the precipitating agent, the rate of formation of the solid complex varied. The complex was filtered off, washed with the precipitating agent and dried to constant mass in vacuum. The complexes were white crystalline powders, stable in air for long storage periods.

For comparison, we also prepared non-complexed PMA (product IV), using the reaction of pyromellitic dianhydride with aniline in acetone at 50° under dry argon. The sediment was filtered off, washed with acetone and dried to constant mass in vacuum. Non-complexed PMA is also a white crystalline powder.

The elemental analysis data correspond to the assumed compositions of the products (Table 1).

Table 1
Elemental analysis of the synthesized compounds

No.	Solvent	Precipitating agent	calcd. C found	calcd. N found	calcd. H found	Composition
I	Dimethylformamide	Benzene	61.09 60.97	10.18 9.99	5.46 5.79	1 PMA · 2 DMF
II	Dimethylformamide	Acetone	61.09 61.32	10.18 9.88	5.46 5.84	1 PMA · 2 DMF
III	Dimethylformamide	Water	62.89 64.76	8.81 7.37	4.82 4.32	1 PMA · 1 DMF
IV	Acetone	—	65.35 64.62	6.93 6.91	3.96 4.33	PMA

PMA = bis(N-phenyl)-pyromellitic diamide

DMF = dimethylformamide

Complex I and the free acid amide IV were investigated by IR spectroscopy in the temperature range 20–110°, in which cyclization of the acid amide group is as yet out of the question. We found that, in contrast to the spectrum of the acid amide IV, the spectrum of complex I shows two frequency shifts with rising temperature: these involve the 1685 cm⁻¹ band, assigned to the bonded DMF, and the 1545 cm⁻¹ band (amide II), assigned to the acid amide component of the complex (Fig. 1). These changes in the spectrum with temperature are reversible. The value of the shift assigned to DMF, the maximum high-frequency shift, is 10 cm⁻¹, while that of amide II, the low-frequency shift, is 5 cm⁻¹. This finding confirms the existence of the PMA–DMF complex in product I, and is evidence of the existence of an equilibrium: complex ⇌ acid amide + DMF.

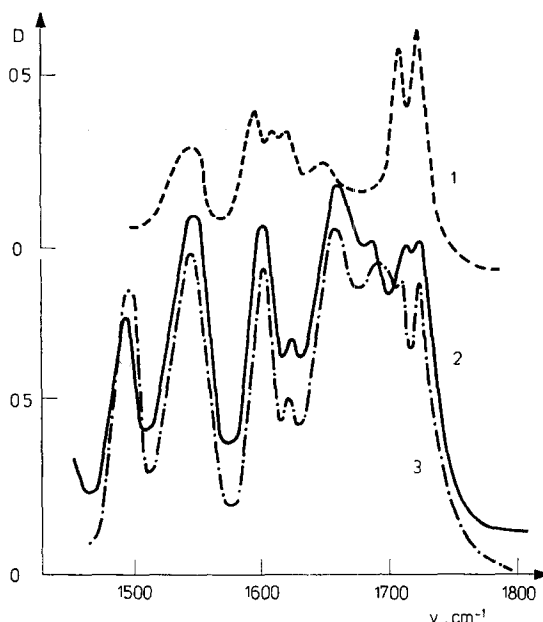


Fig. 1. IR spectra of bis(N-phenyl)-pyromellitic diamide (1) and its complex with dimethylformamide (2 and 3). 1 — in polyethylene matrix, $t = 21^{\circ}\text{C}$, absorption of polyethylene compensated; 2 — $t = 21^{\circ}\text{C}$, 3 — $t = 90^{\circ}\text{C}$. Recorded on the spectrophotometer Spekord 75 IK

Mass-spectrometric thermal analysis

Thermal analysis was carried out at a heating rate of $2^{\circ}/\text{min}$. The glass vial containing the sample was connected to the direct inlet system of the MX-1320 mass-spectrometer by means of a flange. The volatile products evolved on heating of the sample entered the ion source of the mass-spectrometer continuously, and a reading was taken each 1–3 minutes. From these data the thermoanalytical curves were constructed, reflecting the relationship intensity of the ions characterizing the products evolved *vs.* reaction temperature.

Two techniques were used to introduce the PMA–DMP complex sample (mass 2.5 mg) into the vial. In technique 1, the sample is introduced in an open platinum crucible. The decomposition process consequently take place at the working pressure of the mass-spectrometer, that is, around 10^{-5} – 10^{-6} Torr. In technique 2, the sample holder was a special container made of stainless steel. It has a screwed-on lid fitted with an outlet tube containing several holes $15\ \mu\text{m}$ in diameter. In this case, owing to this outlet tube the decomposition process takes place at substantially higher pressures of the volatile products, up to 0.5 bar.

Discussion

The thermoanalytical curves of complex I obtained by technique 1 are presented in Fig. 2. At the beginning of heating, decomposition of the complex and the evolution of DMF took place (curve 1, with maximum at 84°). Subsequently, the PMA molecules broke up and aniline was set free (curve 2, with maximum at 148°). The cyclodehydration process did not take place (no water was observable among the volatile products), and consequently, with increasing temperature, the equilibrium constant of the reaction acid amide synthesis — decomposition will decrease. A similar effect for the reaction proceeding in solution was observed by Ardashnikov *et al.* [4]. Under the high-vacuum conditions of technique 1, ensuring the removal of the relatively volatile aniline, practically complete decomposition of PMA into the initial pyromellitic dianhydride and aniline will take place.

From curve 1, the activation energy of the decomposition of the PMA — DMF complex was found to have a value of 79 ± 9 kJ/mol.

The thermoanalytical curves of complex I obtained by technique 2 are presented in Fig. 3. Curve 2 corresponding to DMF evolution, has two maxima, at 136 and 142°. The maximum values of curve 1, corresponding to the water formed in cyclodehydration, and of curve 3, corresponding to the aniline evolved, are both at 237°. As demonstrated by a comparison of Figs 2 and 3, the decomposition of PMA takes place to a much lesser degree at the higher reaction pressure provided by technique 2. For quantitative determination of the products evolved, we measured the sensitivity of the mass-spectrometer with respect to the volatile products. For this purpose we prepared binary mixtures of DMF and water, and aniline and water, respectively, and recorded their mass-spectra. The calculated relative

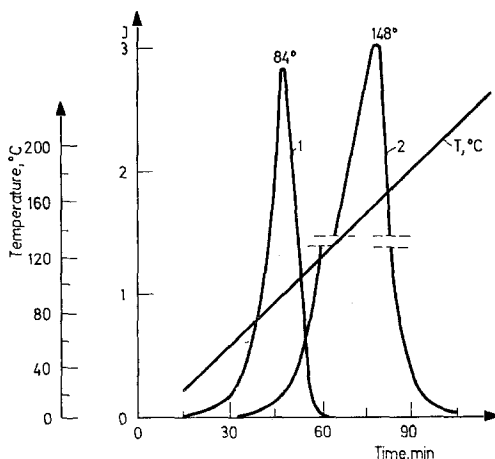


Fig. 2. Mass spectrometric thermoanalytical curves of complex I, obtained by technique 1.
1 — dimethylformamide (mass eq. 73); 2 -- aniline (mass eq. 93)

sensitivity H_2O (mass-eq. 17) to DMF (mass-eq. 73) is 0.24, whereas that of water to aniline (mass-eq. 93) is 0.037. If the decomposition degree of PMA is low, one may assume that the area below curve 3 corresponds to about 2 mols of water evolved per mol PMA.

Taking into consideration the relative sensitivity of the mass-spectrometer with regard to the individual volatile products, a comparison of the areas below the peaks, allows calculation of the amount of DMF evolved per mol PMA, that is, the composition of the complex, and also, based on the amount of aniline evolved, the degree of decomposition of the acid amide bonds. For the case presented in Fig. 3, one obtains that 3.7% of the acid amide bonds were decomposed, yielding the starting materials pyromellitic dianhydride and aniline, and the DMF content in the complex is 2.36 moles per mole PMA. That is, the sample is mainly a complex of composition $\text{PMA} \cdot 2\text{DMF}$. This composition is in conformity with the elemental analysis data for complex I (cf. Table 1).

The thermoanalytical curves presented in Fig. 4 for complex II differ from those in Fig. 3 mainly in that DMF is evolved in one step, with maximum at 134° . The maximum for the peaks corresponding to water and aniline is at 247° . In this case, the decomposition degree of acid amide bonds is estimated as 1.8%, and the amount of DMF evolved is around 2.4 moles per mole PMA, that is the composition of the sample is also close to $\text{PMA} \cdot 2\text{DMF}$, as confirmed by the elemental analysis data.

A very different situation is found with complex III (Fig. 5), obtained with water as precipitating agent. As with the earlier complexes, the first volatile product is DMF (peak maximum at 144°), and subsequently aniline and water (peak maximum at 232°) are evolved. However, a substantially smaller amount of DMF is evolved (0.88 mol per mol PMA). The ratio within the complex closest to this

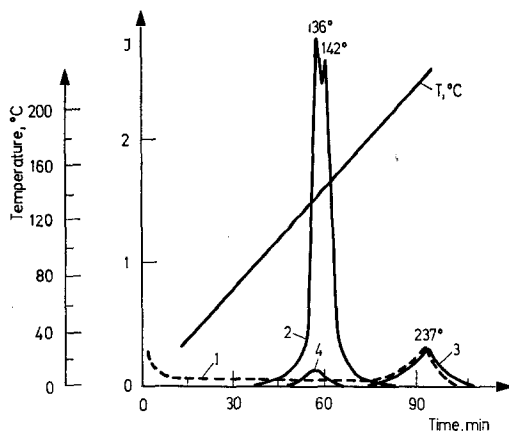


Fig. 3. Mass spectrometric thermoanalytical curves of complex I, obtained by technique 2. 1 — water (mass eq. 17); 2 — dimethylformamide (mass eq. 73); 3 — aniline (mass eq. 93); 4 — benzene (mass eq. 78)

value would then yield a composition PMA . DMF. The decomposition percentage of the acid amide bonds is found to be 2.1%. The elemental analysis data yield an even lower DMF content in the complex (cf. Table 1).

Let us finally examine the thermoanalytical curves of pure PMA (product IV) (Fig. 6). It can be seen that the product contains practically no acetone (curve 1); aniline is evolved with a maximum at 230° and water with a maximum at 210°. The decomposition is significantly higher in this case than in the PMA–DMF complexes, namely 9.5%.

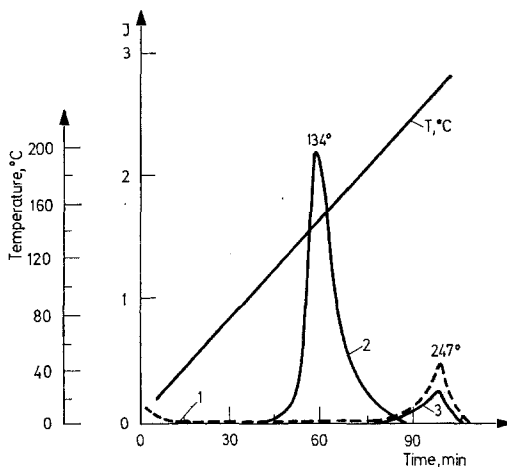


Fig. 4. Mass spectrometric thermoanalytical curves of complex II. 1 — water (mass eq. 17); 2 — dimethylformamide (mass eq. 73); 3 — aniline (mass eq. 93)

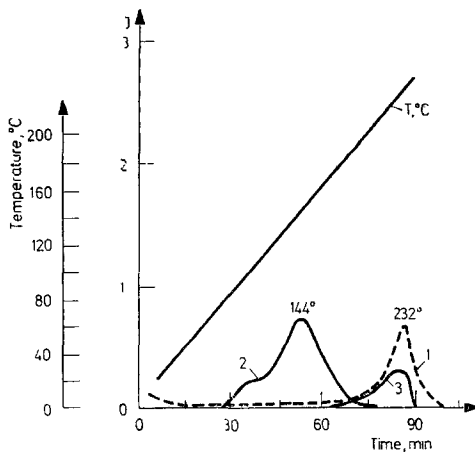


Fig. 5. Mass spectrometric thermoanalytical curves of complex III. 1 — water (mass eq. 17); 2 — dimethylformamide (mass eq. 73); 3 — aniline (mass eq. 93)

From a comparison of the results shown in Figs 3–6, some general conclusions can be made on the cyclodehydration of PMA and on the accompanying processes under the conditions studied.

Firstly, when PMA is synthesized in DMF, a fairly stable PMA–DMF complex is formed, whose composition depends on the nature of the agent used to precipitate the complex from the solution. When this agent is benzene or acetone, the composition of the complex is PMA · 2DMF. When water is used as precipitating agent, a complex with the composition PMA · DMF is formed.

The reasons for this difference are presumably the peculiarities of the structures of the complexes. It is the objective of our further studies to investigate this problem. It is clear from the present results, however, that complexes with different structures are obtained by using different precipitating agents.

One possible explanation of the existence, in Fig. 3 of two different peak maxima for DMF (136 and 142°) in complex I might be the assumption of the existence of “non-symmetric” complexes, that is, the two DMF molecules in the complex are bound in different manners to the PMA molecule. This would involve the action of benzene on PMA during the precipitation of the complex, leading to different orientations of the DMF molecules relative to the PMA molecule when the complex is “set” in the solid state. When precipitating with acetone, one might assume that the latter will act in a different manner in the “setting” process, so that a “symmetric” complex will result, and therefore DMF will be evolved in a single peak, with maximum at 134°. The DMF molecules would then be orientated in the same way relative to the PMA molecule (cf. Fig. 4).

Finally, the interaction of water and PMA is presumably so strong that water will practically displace one molecule of DMF from the complex. As shown in

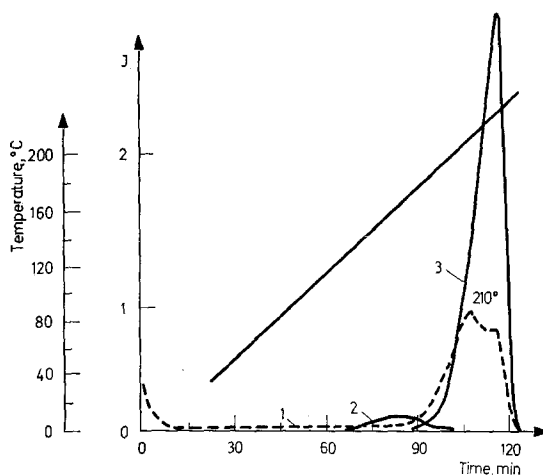


Fig. 6. Mass spectrometric thermoanalytical curves of non-complexed bis(N-phenyl)-pyromellitic diamide (Compound IV). 1 – water (mass eq. 17); 2 – acetone (mass eq. 58); 3 – aniline (mass eq. 93)

Fig. 5, DMF is evolved from this complex in one peak, with maximum at 144° and the composition of the complex is PMA . DMF. It is of interest to note that the site of the maximum in Fig. 4 (134°) coincides with that of the first peak in Fig. 3 (132°), and the maximum in Fig. 5 (144°) with the second peak in Fig. 3 (142°). Relying on these findings, one may presume that two rather sharply separated positions relative to energy exist, in which DMF molecules are capable of complexing with PMA molecules, and that it is the activity of the precipitating molecule which will direct the DMF molecule into the actually occupied position when it attacks the PMA molecule at the moment of precipitation ("setting") of the complex.

Secondly, the effect of complex formation with DMF on cyclodehydration and PMA decomposition (under the conditions of mass-spectrometric thermal analysis is obvious. One can readily observe in Figs 3, 4, 5 and 6 that, in the case of complex, cyclodehydration proceeds at a higher temperature (maxima of the water curves at $232-247^\circ$) and is accompanied by a lower percentage (1.8–3.7%) of decomposition of the acid amide than in the case of pure PMA (water peak maximum 210° and decomposition 9.5%). It is apparent from Figs 3–5 that aniline evolution and cyclodehydration become appreciable only after the nearly complete decomposition of the complex, as if the presence of even slight amounts of the complex suppressed both processes characteristic for PMA at these temperatures. The slighter percentage of acid amide decomposition might be a result of the shift of both reactions into a higher-temperature interval by the presence of DMF, where cyclodehydration will compete more successfully with the decomposition of PMA.

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ZUSAMMENFASSUNG — Komplexverbindungen von Bis(N-phenyl)pyromellitsäurediamiden mit Dimethylformamid wurden synthetisiert und durch thermische Massenspektrometrie untersucht. Es wurde gefunden, daß in Abhängigkeit von dem verwendeten Fällungsmittel die Zusammensetzung der Komplexe den Verhältnissen Acetamid : Dimethylformamid 1 : 2 oder 1 : 1 entsprach. Der Einfluß der Komplexbildung auf die thermische Cyclodehydratisierung von Bis(N-phenyl)pyromellitsäurediamid und auf die begleitenden Zersetzungs Vorgänge wird diskutiert.

Резюме — Синтезированы и исследованы методом масс-спектрометрического термического анализа комплексы бис-(N-фенил)-пиромеллитамидокислоты (ПМК) с диметилформамидом (DMF). Показано, что в зависимости от применяемого осадителя, комплексы могут иметь состав: 1 ПМК : 2 ДМФ и 1 ПМК : 1 ДМФ. Обсуждено влияние комплексообразования на протекание термической циклодегидратации ПМК и сопутствующих ей процессов распада.